Appendix
Calibration of $\delta O_2/N_2$ measurements

Abstract

This appendix includes the description of the calibration procedures used for the $\delta O_2/N_2$ measurements as presented in this thesis. This covers both the measurements by the Micromass Optima dual inlet isotope ratio mass spectrometer (DI-IRMS) and the continuous measurements by the Oxzilla II fuel cell analyzer.

A.1. Calibration of the air optima*

A.1.1. In general

The air optima has been described in chapter 2, and the $\delta O_2/N_2$ measurements of flask samples measured by this Micromass Optima dual inlet isotope ratio mass spectrometer (DI-IRMS) are presented in chapters 4 and 5. The air optima has also been used to establish the $\delta O_2/N_2$ ratio of the calibration cylinders used for the continuous O_2 measurements by the Oxzilla II as presented in chapter 3. The calibration of the Oxzilla is discussed further on, in section A.2.

The air optima measures each sample against the machine gas. This gives the $\delta O_2/N_2$ ratio, as shown in equation A.1 (comparable to isotope δ values and explained in earlier chapters).

$$\delta(O_2/N_2) = \frac{(O_2/N_2)_{sample}}{(O_2/N_2)_{machine\ gas}} - 1 \qquad (A.1)$$

Each measurement consists of 7 delta values which are used to establish a more precise average value. These 7 measurements are first filtered to exclude a maximum of 2 outliers, using an "exclusive" outlier filter. This filtering procedure first calculates the average and the standard deviation of the 7 measurements. Next, the measurement which is the farthest from the average is hypothesized to be an outlier. To test this hypothesis, the average and standard deviation are calculated of the remaining 6 measurements. We define our hypothesis to be proven if the 7^{th} measurement was more than 2.7 times the new standard deviation away from the new average. If this is the case, the measurement is excluded. The procedure is then repeated to identify a possible second outlier. The final $\delta O_2/N_2$ ratio against the machine gas is then the average of the remaining measurements.

This thesis contains measurements of the air optima between 1998 and 2009. During this period 6 different machine gases were used. The length of the period during which a machine gas was used, varied between a few months and several years. Table A.1 shows an overview of the used machine gases and the periods in which they were used.

*The isotope calculations in this section are based on the content of Mook (2001).

Table A.1: Overview of the machine gas and local reference gas cylinder numbers used for the calibration of the air optima.

Period		Machine gas	Local reference gas(es)
1	17-08-1998 – 18-02-2000	2534	4497
2	19-06-2000 – 17-11-2003	4497	4446
3	03-02-2004 – 18-02-2004	4446	8780
4	18-02-2004 – 14-05-2004	8780	4446
5	04-06-2004 – 19-10-2005	4866	2534
			7512
			8780
6	30-01-2006 – 20-11-2009	6170	2534
			5279
			6096
			6168
			6987
			8780

The local reference gases were used to correct for drifts of the instrument. As shown in table A.1 the number of local reference gases has increased from only one during the initial measurement period up to 6 in the latest period. As discussed in chapter 4, the latest data is therefore more accurate than the earlier data. A scale conversion is required for each time the machine gas has been changed. The data in chapters 4 and 5 is presented against the Scripps Institution of Oceanography (SIO) scale. The SIO primary cylinders were available from period 6 and therefore, only during the current machine gas the six local reference gases could be established on the SIO scale directly (since the SIO primary cylinders were measured against the same machine gas). The calculation of the data and the scale conversions therefore start in the latest period and are calculated backwards to the initial period.

A.1.2. The period 2006-2009

Figure A.1 shows all measurements of the local reference gases during period 6 (including those identified as outliers, see further on). The darker symbols represent the raw measurements and the lighter ones indicate the drift corrected values against the Scripps Institution of Oceanography (SIO) scale. Period 6 has been divided into three parts. The three SIO cylinders were measured during the second and third part of this period.

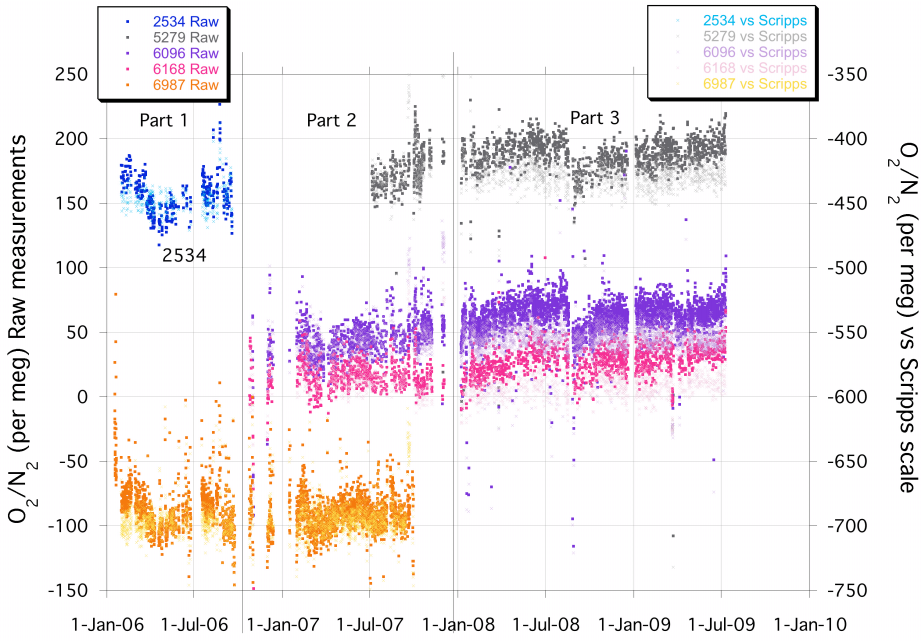

Figure A.1: The measurements of the local reference gases during period 6. During this period the machine gas was cylinder 6170.

The measurements performed by the air optima are influenced by a "zero-enrichment" factor. This implies that the measurements of a certain local reference gas against the machine gas do not yield the same result as when they were measured the other way around. As explained above, the δ values in isotope measurements are calculated by equation A.1, using the O_2/N_2 ratio (R). Equation A.2 through A.4 show the general relationships between sample (S) versus reference (R) measurements and reference versus sample measurements when there is no "zero-enrichment" factor. Equation A.5 shows the relationship including the "zero-enrichment" factor (Z).

General isotope calculations:

$$\delta_{S/R} = \frac{R_S}{R_R} - 1 \Rightarrow \frac{R_S}{R_R} = \delta_{S/R} + 1 \tag{A.2}$$

$$\delta_{R/S} = \frac{R_R}{R_S} - 1 \Rightarrow \frac{R_R}{R_S} = \delta_{R/S} + 1 \Rightarrow \frac{R_S}{R_R} = \frac{1}{\delta_{R/S} + 1} \tag{A.3}$$

$$\delta_{S/R} = \frac{1}{\delta_{R/S} + 1} - 1 \tag{A.4}$$

$$\delta_{S/R} = \frac{1}{\delta_{R/S} + 1} - 1 + Z \tag{A.5}$$

As the "zero-enrichment" factor can change overtime, it is not sufficient to know the calibrated value of the machine gas. Instead, one of the local reference gases, which is treated identical to the samples, was used as the basis of the calibration procedure. Therefore all measurements are expressed as the difference to this gas, which now acts as the reference gas. Cylinder 2534 has been chosen to serve as the principal local reference gas, as it has lasted the longest and was measured during several machine gas periods (see table A.1). So, all raw measurements against the machine gas are first expressed against cylinder 2534, and after that recalculated against the Scripps cylinders.

Figure A.1 also shows a partitioning in three parts. These are separated due to changes in the local reference gases accompanied by a (small) jump in the averages between these periods. The jumps are corrected for by shifting the average values of the local reference gases, starting from part 1, since this is the period with the measurements of cylinder 2534, and then continuing to part 2 and 3.

On top of the "zero-enrichment" factor, the measurements on the air optima also experience drifts over time. This is visible in figure A.1 for period 6. The darker symbols are the raw measurements which are not stable during the entire period. To implement a drift correction, period 6 is divided into 27 sub-periods, characterized by e.g. a gap in the data series, a change in the drift, a jump, a failure of the machine etc. After that, the measurements of each local reference standard are averaged individually. Next, outliers are excluded from the data using the exclusive outlier filtering procedure. After that, for all measurements of each local reference standard, its average is subtracted from the respective data series, so that all data series lay around 0. Now the measurements of the different local reference gases can be used together to obtain a possible jump or drift in each sub-period.

In sub-periods with no (significant) drift during the sub-period, the data are filtered based on the average of the measurements in that sub-period. In case the average value of the sub-period is different from the average of the total period, the values are corrected based on the average only. In case the data in a sub-period experience a drift, the linear trend of this drift is obtained by a linear fit. The residuals of this fit are again filtered for outliers. After that, a new linear trend is obtained for this sub-period. The corrections for the data within the specific sub-period explained further on.

Figure A.2a shows an example of a sub-period with a drift (sub-period 24). The data point are the values for local reference gas cylinders 5279, 6096 and 6168 together, shifted to average 0 based on their individual averages. The drift in this sub-period is visible in the data series for all three local reference gases, which is why the linear trend can best be obtained using the data from all three local reference gases together. The drift is corrected for using a linear trend, which is indicated in the figure. The drift corrected values for the three local reference gases together are shown in figure A.2b (still as the values shifted to 0). Figure A.2c shows the corrected values for the local reference gas cylinder 6168 presented as its values against the machine gas 6170.

a

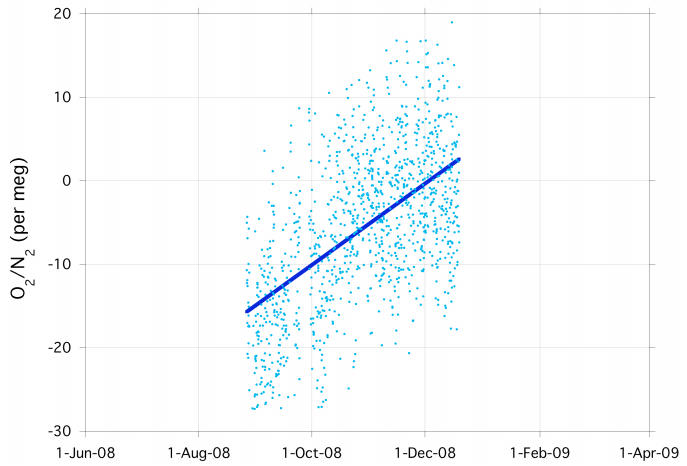

Figure A.2: An example of sub-period 24 within machine gas period 6. The graph shows the measurements of three local reference gases shifted to zero based on their individual averages within part 3 of period 6 (a).

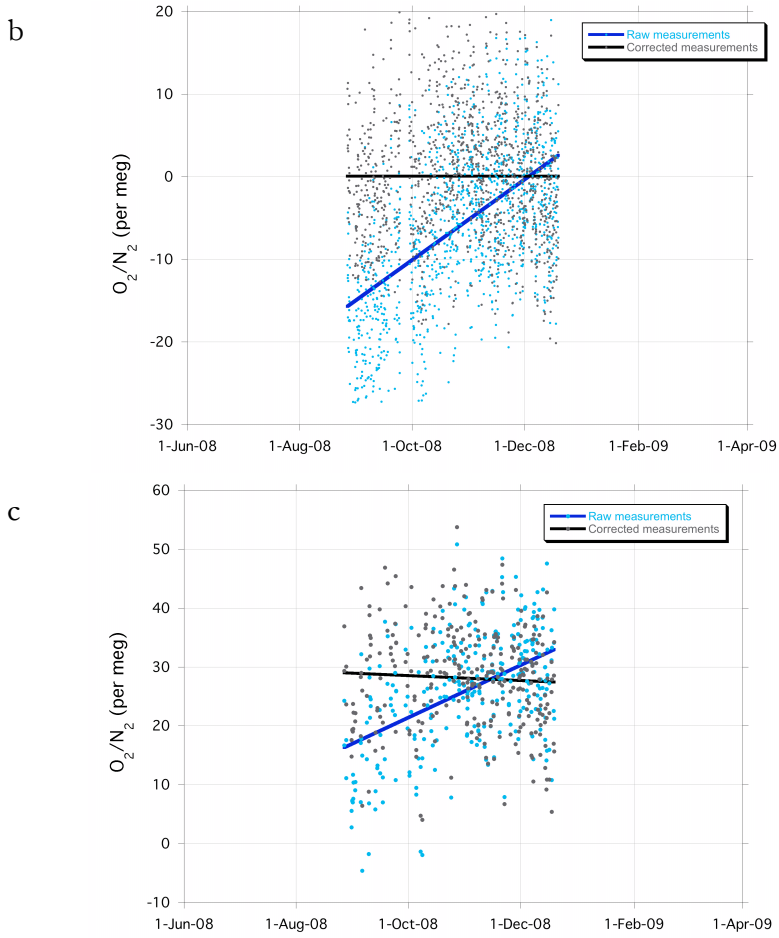

Figure A.2 (continued): An example of sub-period 24 within machine gas period 6. The graph shows the measurements of three local reference gases shifted to zero based on their individual averages within part 3 of period 6 (a), the raw and corrected values for all measurements (b) and for the local reference gas cylinder 6168 only (c).

Apart from correcting for drifts, all measurements need to be calibrated to an identical scale. For this purpose, all data is first assessed as the difference between the measurement and the measurement of local reference gas cylinder 2534 on the sample side. In period 6, 2534 is measured as a sample (i.e. local reference gas) in the first part (see figure A.1). Equation A.6 through A.8 show in general how to calibrate a sample (S) measured against a machine gas (M) to another scale (R).

$$\delta_{M/R} = \frac{R_M}{R_R} - 1 \quad \Rightarrow \quad R_R = \frac{R_M}{\delta_{M/R} + 1} \tag{A.6}$$

$$\delta_{S/M} = \frac{R_S}{R_M} - 1 \quad \Rightarrow \quad R_S = R_M \cdot (\delta_{S/M} + 1) \tag{A.7}$$

$$\delta_{S/R} = \frac{R_S}{R_R} - 1 = \frac{R_M \cdot (\delta_{S/M} + 1)}{R_M / (\delta_{M/R} + 1)} - 1 = (\delta_{S/M} + 1) \cdot (\delta_{M/R} + 1) - 1 \tag{A.8}$$

Equation A.9 is used to include both the drift correction and the shift to the 2534 scale (R) for measurement in a certain sub-period.

$$\delta_{S/R} = \left((\delta_{M/R})_{\text{sub-period}} + \text{drift}_{\text{per day}} \cdot \frac{\text{days}}{365} + 1 \right) \cdot (\delta_{S/M} + 1) - 1 \tag{A.9}$$

The $\delta_{M/R}$ value for the sub-period can have two alternative meanings. In the case that the drift equals zero, $\delta_{M/R}$ is the average value of the local reference gas against the machine gas during the specified sub-period, whereas in case the drift does not equal zero the value of $\delta_{M/R}$ is the value at the beginning of the drift in the sub-period. The calculation of $\delta_{M/R}$ for a certain sub-period in which the drift is zero is calculated using the measurements of the local reference gas (L) as shown in equation A.10.

$$(\delta_{M/R})_{\text{sub-period}} = \frac{(\delta_{L/M} + 1)_{\text{average total}}}{(\delta_{L/M} + 1)_{\text{sub-period}}} \cdot (\delta_{M/R} + 1)_{\text{total}} \tag{A.10}$$

In period 6, the values for $\delta_{L/M}$ for the total and the sub-period are calculated using multiple local reference gases as explained above, which are shifted to zero. The $\delta_{M/R}$ value for the total period is calculated using equation A.11, where M is the machine gas 6170 and R is cylinder 2534.

$$\delta_{M/R} = \frac{1}{\delta_{R/M} + 1} - 1 \tag{A.11}$$

The drift used in equation A.9 is calculated per day as the drift of $\delta_{M/R}$ and the days since the beginning of the sub-period are used to calculate the "virtual" value of $\delta_{M/R}$ at the moment of the measurement. To calculate the drift of $\delta_{M/R}$, the value of $\delta_{L/M}$ at the beginning and the end of the sub-period are calculated using equation A.12, which is equivalent to equation A.10.

$$(\delta_{M/R})_{\text{begin}} = \frac{(\delta_{L/M} + 1)_{\text{average total}}}{(\delta_{L/M} + 1)_{\text{begin}}} \cdot (\delta_{M/R} + 1)_{\text{total}} \tag{A.12}$$

The value of $\delta_{L/M}$ at the end of the sub-period is calculated in the same way, which gives the value of the drift $\delta_{M/R}$.

A.1.3. The period between June 2004 and January 2006

The corrections and calibration procedures applied to period 6, as described in the previous section apply identically to period 5 including the division in sub-periods, only no partitioning in parts has been made in this period, since the local references were the same during the entire period. The local reference gas 2534 has also been measured in period 5, which enables a direct calculation of the difference of the other local reference gases to cylinder 2534. Figure A.3 shows the measurements of the local reference gases in period 5, both as raw measurements and as after corrected and calibrated.

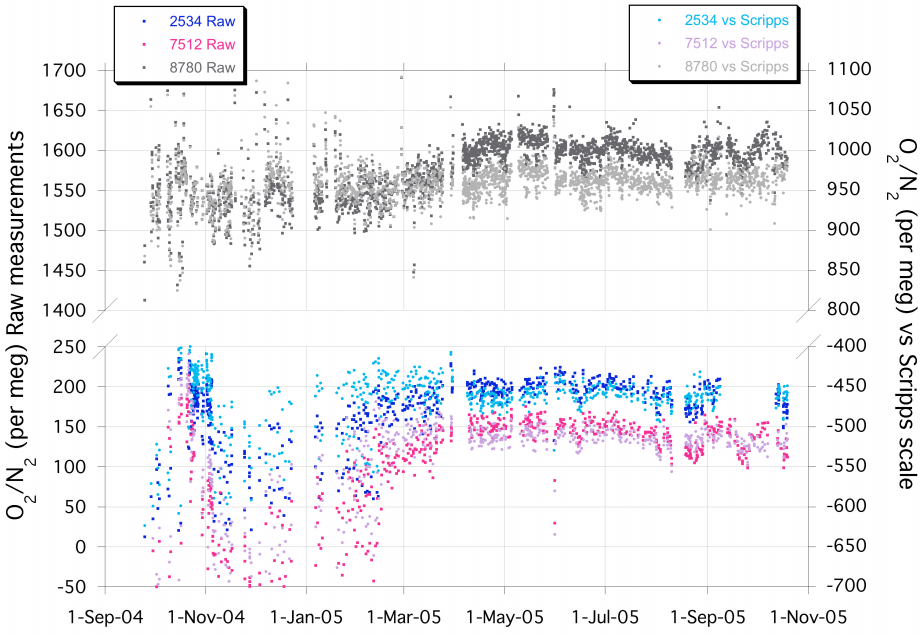

Figure A.3: The measurements of the three local reference gases during period 5. During this period the machine gas was cylinder 4866. The figure shows the raw measurements together with the corrected values against the Scripps scale.

A.1.4. Prior to June 2004

Periods 1 through 4 are less well established than periods 5 and 6, for two reasons. Firstly, the local reference gas cylinder 2534 was not measured as a sample in these four periods. Secondly, in these four periods only 1 local reference gas was measured along with the samples. As shown in table A.1, in period 3 and 4, the machine gas and the local reference gas are reversed. The measurements in periods 3 and 4 can therefore be used to calculate the zero-enrichment factor, assuming that the zero-enrichment factor was constant throughout these periods. The procedure for filtering outliers from the local reference gas measurements and corrections within sub-periods is identical to that for period 5 and 6, as described above. Figure A.4 shows the raw measurements of the local reference gas cylinder in periods 3 and 4 together with the corrected values against the Scripps scale.

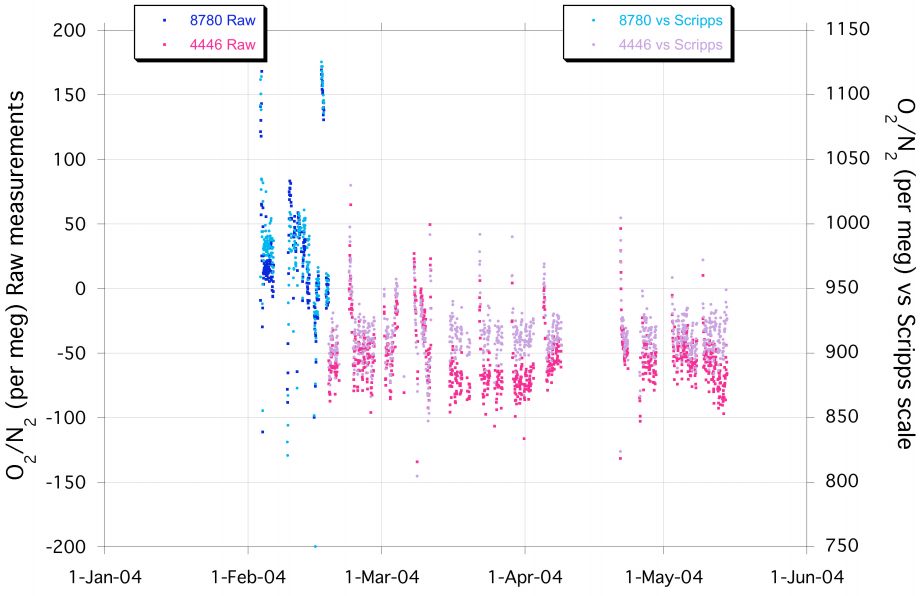

Figure A.4: The measurements of the local reference gases during periods 3 and 4. During period 3 the machine gas was cylinder 4446 and the local reference gas was 8780. In period 4, this was reversed: the machine gas was 8780 and the local reference gas was 4446. The figure shows the raw measurements together with the corrected values against the Scripps scale. The legend indicates the local reference gas which is measured (as in the previous graphs).

The average of the (filtered) measurements of the raw measurements of local reference gas 8780 versus machine gas 4446 in period 3 was 27.7 ± 3.1 per meg. In period 4, the average of the filtered measurements of local reference gas 4446 versus machine gas 8780 was -55.4 ± 0.6 per meg. These numbers are used to estimate the zero-enrichment factor at -13.9 ± 1.6 per meg. Cylinder 8780 was measured in period 5 as a local reference gas together with cylinder 2534. The value of 8780 versus 2534 for period 5, together with the zero-enrichment factor are used to correct and calibrate the measurements in period 4 against cylinder 2534 using $\delta_{M/R}$ from equation A.13, which is a modified version of equation A.10.

$$(\delta_{M/R})_{sub-period} = \frac{(\delta_{L/M} + 1)_{average\ total}}{(\delta_{L/M} + 1)_{sub-period}} \cdot \frac{(\delta_{M/R} + 1)_{period\ 5}}{(zero + 1)} \qquad (A.13)$$

In period 3, the local reference gas was 8780, so the calculation of the corrected values against 2534 can be transferred through cylinder 8780 and the zero-enrichment factor is not required. Equation A.14 shows the correction and calibration for period 3.

$$(\delta_{M/R})_{sub-period} = \frac{(\delta_{L/M} + 1)_{average\ total}}{(\delta_{L/M} + 1)_{sub-period}} \cdot (\delta_{M/R} + 1)_{period\ 5} \qquad (A.14)$$

This is comparable to period 5 and 6, except that the value for $\delta_{M/R}$ is not measured in the same period, but in period 5.

In period 2, the local reference gas was 4446, which was the machine gas in period 3 and the local reference gas in period 4. The machine gas 4497 was not measured after period 2. The only connection between the measurements in period 2 and the later periods is therefore the local reference gas 4446. All calibrations are done starting from period 6, since the Scripps cylinders were measured only during that period. The correction and calibration equation therefore includes again the zero-enrichment factor as shown in equation A.15.

$$(\delta_{M/R})_{sub-period} = \frac{(\delta_{L/M} + 1)_{average\ total}}{(\delta_{L/M} + 1)_{sub-period}} \cdot (\delta_{M/R} + 1)_{period\ 2} \cdot (zero + 1) \qquad (A.15)$$

$\delta_{M/R}$ cannot be obtained directly in this case, as cylinder 4497 has not been measured together with cylinder 2534. The calculation of $\delta_{M/R}$ (or $\delta_{4497/2534}$) is shown in equation A.16.

$$(\delta_{M/R})_{period\ 2} = \delta_{4497/2534} = \frac{(\delta_{4446/2534} + 1)_{period\ 4}}{(\delta_{4446/4497} + 1)_{period\ 2} \cdot (zero + 1)} \qquad (A.16)$$

The value for $\delta_{4446/2534}$ in period 4 is calculated using equation A.17.

$$\delta_{4446/2534} = \frac{(\delta_{4446/8780} + 1)_{\text{period 4}}}{(\text{zero} + 1)} \cdot (\delta_{8780/2534} + 1)_{\text{period 5}} \qquad \text{(A.17)}$$

The raw measurements together with the corrected and calibrated values are shown in figure A.5.

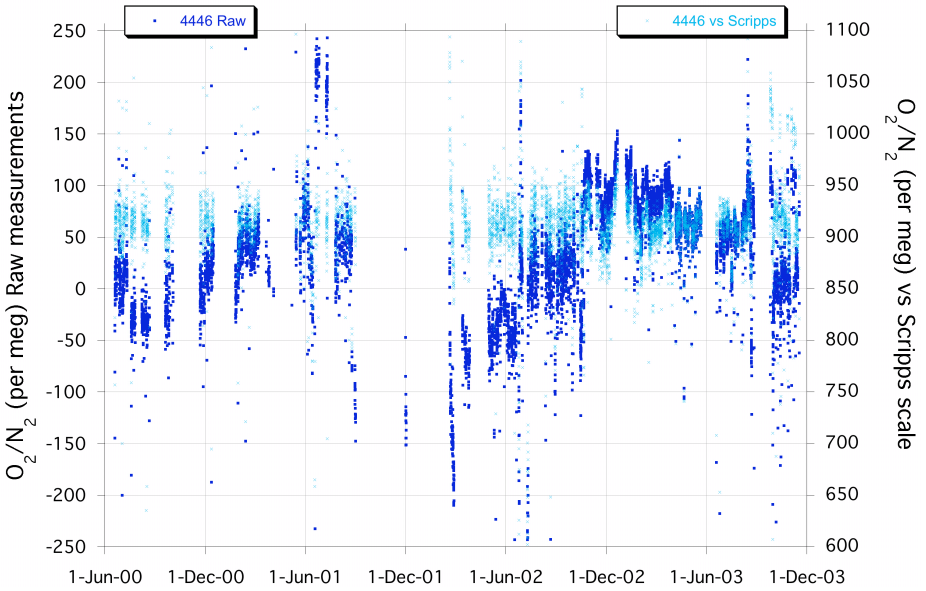

Figure A.5: The measurements of the local reference gas 4446 during period 2 against machine gas 4497. The figure shows the raw measurements together with the corrected values against the Scripps scale.

The first measurement period, period 1, is calculated ultimately. As these measurements are farthest from the measurements of the primary Scripps cylinders, the accuracy of these measurements is lowest. For the correction of the measurements in period 1, the value of $\delta_{4497/2534}$ as calculated for period 2 is used. Equation A.18 shows the correction and calibration for the measurements in period 1.

$$(\delta_{M/R})_{\text{sub-period}} = \frac{(\delta_{L/R} + 1)_{\text{period 2}}}{(\delta_{L/M} + 1)_{\text{sub-period}}} \qquad \text{(A.18)}$$

Where $\delta_{L/R}$ from period 2 is equal to the value of $\delta_{4497/2534}$ as calculated for period 2 (see equation A.16). The raw and corrected and calibrated values for period 1 are shown in figure A.6.

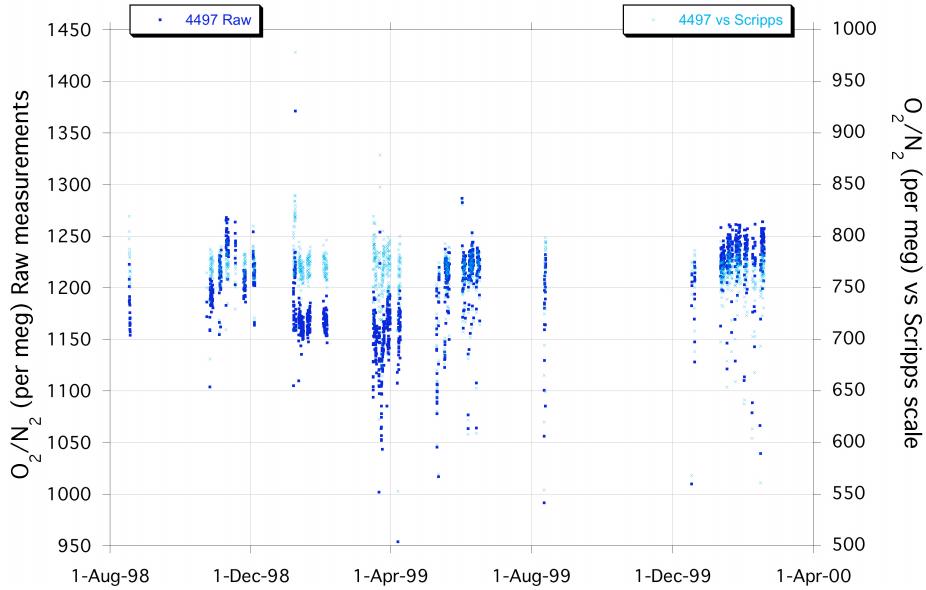

Figure A.6: The measurements of the local reference gas 4497 during period 1 against machine gas 2534. The figure shows the raw measurements together with the corrected values against the Scripps scale.

The calibration procedure as described in this section has been calculated backwards starting in 2009 down to 1998. The difference between the average $\delta_{4497/2534}$ value as calculated using information from the subsequent periods is 1314 per meg. The average of the measurements of $\delta_{4497/2534}$ in period 1 is 1198 per meg. In the first case, the $\delta_{4497/2534}$ value is the difference between the measurements of both cylinders on the sample side of the instrument, whereas in the second case, cylinder 2534 was serving as a machine gas. This difference in the definition of the $\delta_{4497/2534}$ value together with the fact that the zero-enrichment factor of the instrument is likely to have changed over time, accounts for this difference.

A.1.5. Overview of the calibration of the air optima

Figures A.7 and A.8 show an overview of the raw measurements of all local reference gases against the machine gas of the specific period between 1998 up to 2009 together with the corrected and calibrated values presented on the Scripps scale. From these figures it is clear that the precision of the measurements has improved significantly during the period it has been operational. The improvement in the accuracy over time is not visible from the figure, only the fact that more local reference gases are measured to obtain the calibrated values. The measured samples presented in this thesis have been treated identically to the local reference gases to obtain their final values.

Table A.2 shows an overview of the estimated precision and accuracy of the measurements of the air optima for the 6 machine gas periods. The estimates for the precision are based on the spread of the corrected measurements of the working gases as shown in figure A.8. The local reference gases are first filtered and then the standard deviation of the entire period is obtained. The standard deviation is divided by √2 as the flasks are generally measured twice. The accuracy indicated in table A.2 is the estimated extra uncertainty introduced by the required scale conversion for the change of the machine gas. The extra uncertainty increases from period 6 to period 1, so the 6 per meg extra uncertainty between period 6 and 5 is also present in the previous periods. These estimates are based on the difference in the average of the local reference cylinders measured in both periods.

Table A.2: Overview of the precision and accuracy of the measurements of the air optima during the 6 difference machine gas periods.

Period	Machine gas	Precision (per meg)	Accuracy (per meg)
1	2534	8	15
2	4497	13	15
3	4446	17	10
4	8780	9	15
5	4866	11	6
6	6170	6	3

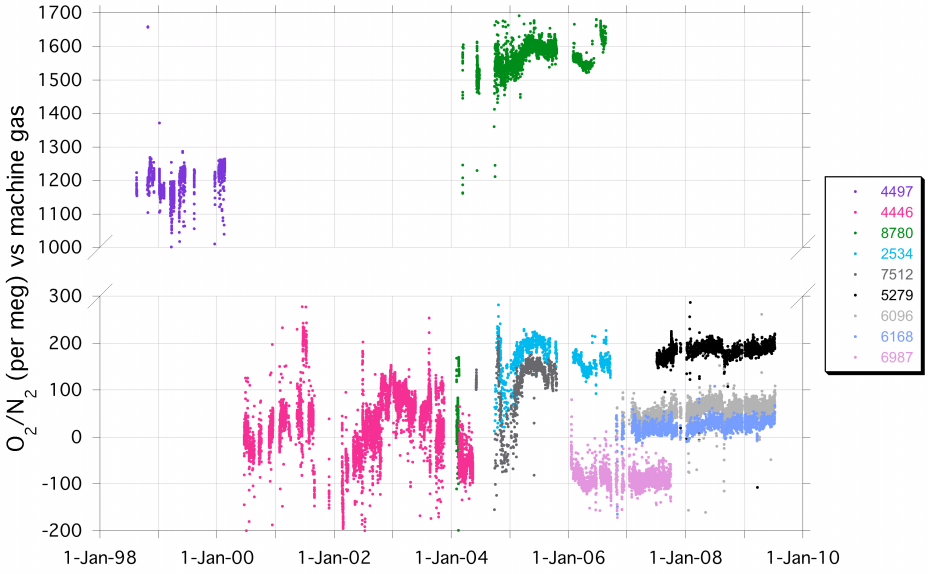

Figure A.7: An overview of the raw measurements of all local reference gases against the machine gas of the period they were measured in.

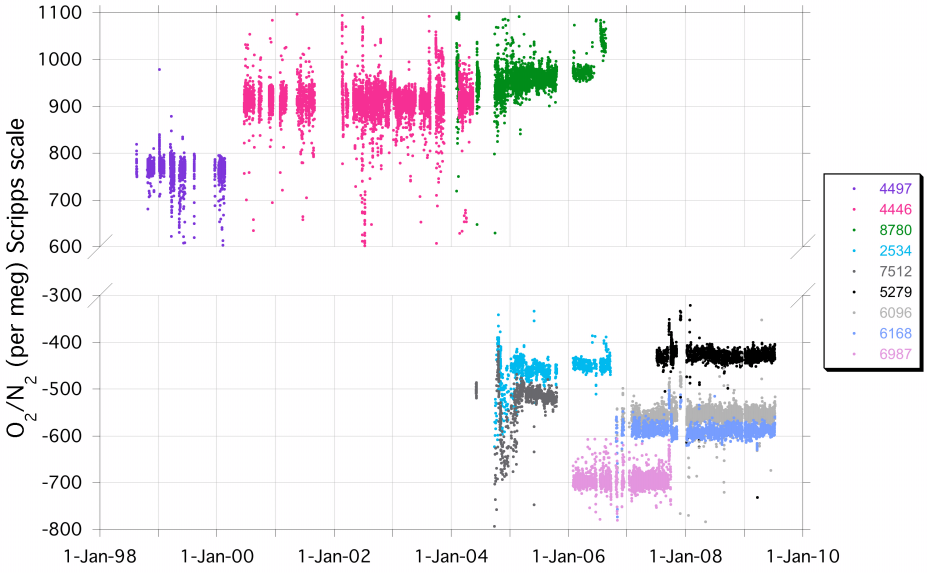

Figure A.8: An overview of the corrected and calibrated values of the measurements of all local reference gases presented on the Scripps scale.

A.1.6. Results from the air optima: O_2 data from Mace Head

The previous sections have shown the calibration procedures as used for the data measured by the air optima. The air optima is configured to measure flask samples. The flasks measured are collected at several locations around the world by the Centre for Isotope Research and collaborative partner institutes. This section shows additional insights for the results from the flask samples from Mace Head, Ireland as presented in chapter 4 in light of the calibration of the air optima, specifically related to the 6 machine gas periods. Figure A.9 shows the O_2 data series for Mace Head, which is a modified version of the data series presented in figure 4.3b. The different colours of the data points indicate the machine gas of the respective period during which the specific flask was measured. Figure A.9 includes all valid data points, including those defined as outliers as described in chapter 4.

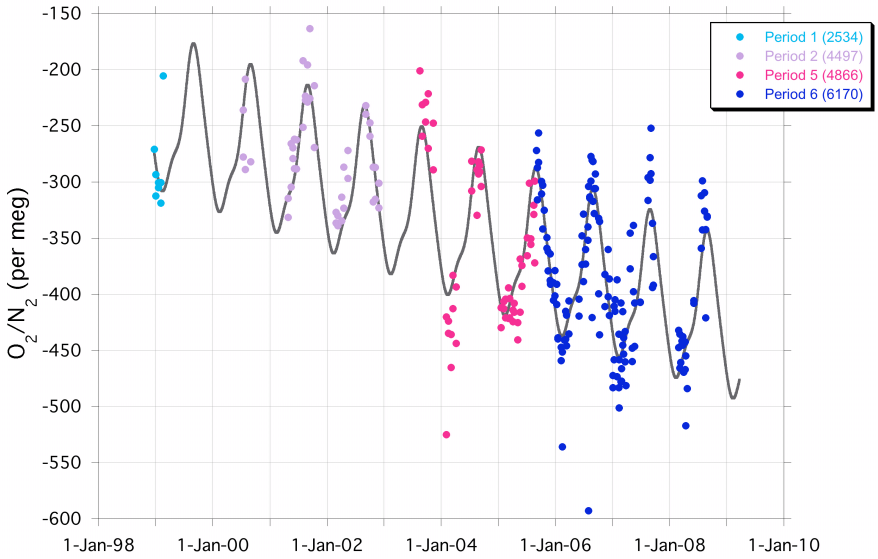

Figure A.9: The observations of atmospheric O_2 from Mace Head, Ireland. The different colours of the data points indicate the machine gas of the respective period during which the specific flask was measured.

The flasks from Mace Head were measured only during 4 out of 6 of the machine gas periods. The figure shows that the data from all 4 periods corresponds well with the trend fit, in spite of the lower accuracy in the first two periods. The accuracy of the measurement from the first two periods could, however, influence the uncertainty in the trend estimates as presented in chapter 4 and 5.

Figure A.10 shows the residuals to the fit for the Mace Head observations against the amount of days between the sample was taken and the date of the measurement on the air optima. The 4 different machine gases are again indicated with different colours. The outliers as excluded from the time series as presented in chapter 4 are indicted with open symbols. Even though they also include synoptic variations, the scatter in the residuals and the presence of outliers can be used as indicators for the measurement quality. The average time between the sample date and the measurement date for the Mace Head flask samples is 327 days. Storage of flasks samples can influence the $\delta O_2/N_2$ ratios after some time, this effect has been described by Sturm et al. (2004). The data in figure A.10, however, do not show an increase in the residuals to the fit, nor a correlation between the amount of outliers and the elapsed time. From the Mace Head flask samples, a negative effect between the elapsed time and the measurement quality can therefore not be confirmed. There is also no indication from figure A.10 that the data in the earlier machine gas periods (2534 and 4497) are of poorer quality than the data measured in the later machine gas periods.

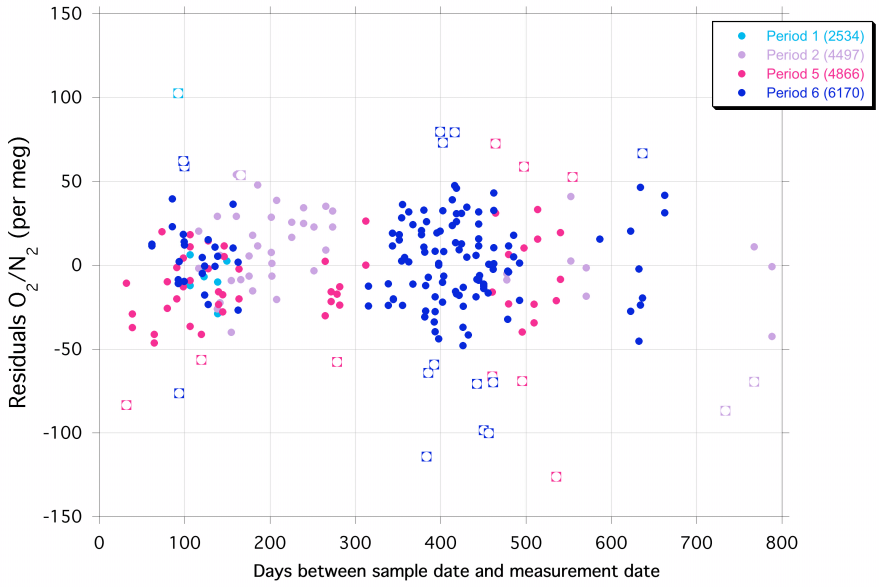

Figure A.10: The residuals to the fit for the Mace Head observations against the number of days between the sample date and the measurement date on the air optima. The different colours represent the 4 different machine gas periods. The open symbols are measurements which have been identified as outliers in chapter 4.

A.2. Calibration of the Oxzilla

The continuous measurements performed with the Oxzilla II as presented in chapter 3, have been calibrated using reference gases of which the $\delta O_2/N_2$ ratios have been obtained by the air optima mass spectrometer. The continuous $\delta O_2/N_2$ measurements from the F3 platform have been calibrated using the calibration gases and reference gases as presented in table A.3.

Table A.3: Overview of the calibration and reference gas cylinder numbers used for the calibration of the Oxzilla.

Period		Calibration	Target	Reference
1	25-08-2008 – 14-09-2008	8577 & 9570	4866	7888
2	16-09-2008 – 08-10-2008	8577 & 9570	4866	9580
3	10-10-2008 – 07-11-2008	8577 & 9570	x	9580
4	07-11-2008 – 06-12-2008	8577 & 9570	9626	9633
5	24-12-2008 – 14-01-2009	8577 & 9570	9626	9582
6	19-03-2009 – 01-04-2009	8577 & 9570	9626	9633
7	01-04-2009 – 22-04-2009	8577 & 9570	9626	1398
8	22-04-2009 – 10-05-2009	8577 & 9570	9626	6987
9	21-05-2009 – 14-06-2009	8577 & 9570	9626	4446

The differential measurements of the Oxzilla are given as $\Delta(\Delta)$ values (see chapter 1 and 3 for more details) and expressed in % O_2. The $\Delta(\Delta)$ values are a measure for the difference between the measured sample and the reference gas (which is also continuously measured). Two calibration gases are measured on a 23 hour basis, following the identical procedure as the samples. In all periods except period 3, a target cylinder was measured along with the two calibration cylinders, to serve as a "known unknown", yielding independent information about the measurement stability, accuracy and precision.

The $\Delta(\Delta)$ values of the calibration gases measured by the Oxzilla are used to construct a linear calibration line. As explained in chapter 1 and 4, O_2 values are expressed as $\delta O_2/N_2$ ratios, even if they are measured as % O_2 values. In order to convert the measured $\Delta(\Delta)$ values to $\delta O_2/N_2$ ratios, the O_2 mole fraction is used, as this is an absolute variable. Equation A.19 shows the relationship between $\delta O_2/N_2$ and δXO_2 (the O_2 mole fraction).

$$\delta(O_2/N_2) = \frac{\delta XO_2 + (\Delta CO_2 \cdot S_{O_2})}{(1 - S_{O_2}) \cdot S_{O_2}} \quad \text{(in per meg)} \qquad \text{(A.19)}$$

S_{O_2} = 0.20946 and ΔCO_2 = [CO_2] – 363.29 (ppm), as described in earlier chapters. The CO_2 concentration of the calibration cylinders is obtained by measurements on the GC (see chapter 2). Equation A.19 is used to obtain the δXO_2 values for the calibration cylinders. Each reference gas period has its specific parameters for the linear calibration line. These parameters are obtained by repeated measurements of the calibration gases against the same reference gas. An example of the linear calibration line for period 8 (see table A.3) is shown in figure A.11. The $\Delta(\Delta)$ values for the calibration gases are obtained by taken the averages of the final 15 minutes for each measurement period of the calibration gas during the specific reference gas period. This procedure is in principle of poorer quality than determining a new calibration line after each new measurement of the calibration gases after 23 hours. However, the measurement precision of the Oxzilla has been less precise than the variations within a few months, which is why the averaging of the measurements of all calibration gases within a reference gas period, gives more precise results. This conclusion was reached after analysis of the measurements of the target cylinder (see chapter 3). The calibration of the CO_2 measurements by the CarboCaps is identical, only no conversion is necessary and the measured CO_2 concentrations of the calibration cylinders by the GC can by used on the y-axis of the calibration graph directly.

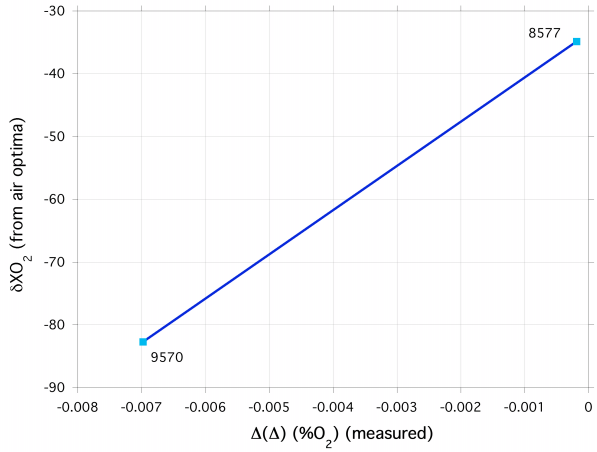

Figure A.11: An example of a linear calibration line for the Oxzilla O_2 measurements (in measurement period 8).

References

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